X-ray Induced Luminescence of the Noble Gases at High Pressure

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Introduction

The noble gases are some of the simplest systems available for electronic and optical studies at high pressures. Yet, little has been investigated concerning the luminescence of the condensed noble gases in the visible region.[1] This is especially true with respect to high pressures.[2] The ability to probe the noble gases by x-ray excitation in a diamond-anvil cell is an invaluable tool for understanding the effects of pressure on the electronic structure of atoms.

In this study, we observed the x-ray induced visible luminescence of argon, krypton and xenon up to 60 GPa. The intense, well-collimated x-ray source and beryllium window optics, both present at GeoSoilEnviroCARS, (GSECARS), are required to illuminate the microscopic sample and collect the emission.

Method and Materials

Noble gases are condensed into either their solid (krypton and xenon) or liquid (argon) state at low temperature and then subsequently trapped and contained in the aperture of a gasketed diamond anvil cell. Typically the sample will have a diameter of ~100 µm. A few ruby chips (~5 mm) will be preloaded inside the aperture as a pressure sensor.

The x-rays are collimated to 10 µm and illuminate a small area of the sample. A monitor is used to display a CCD camera image of this sample. Typically, the luminescence is very intense. However, we have noted that not all regions of the sample are equally bright. Emission is collected by using a beryllium window to reflect the luminescence towards a lens that focuses the light into a fiber-optic guide. The other end of the fiber is connected to a reflecting telescope mated to a spectrometer with a liquid-nitrogen-cooled CCD detector. A spectrum covering the entire visible range with high-quality signal to noise can be obtained within a few seconds. The fiber, due to light scattering, effectively acts as a short-wave cut-off filter around 400 nm.

Pressures can be measured by using the ruby luminescence technique or by taking the energy-dispersive x-ray diffraction or angle-dispersive x-ray diffraction pattern of the rare gas and using the known equation of state.

Results

A series of luminescence spectra are obtained at intervals of 3 to 5 GPa. The luminescence peaks are fit to Lorentzian lineshapes. Examples are shown in Fig. 1. The peak positions are observed to shift with pressure. Figure 2 (next page) summarizes these results for argon and krypton. In the case of xenon, however, the shift appears to be very rapid over a small region of pressures and can not be meaningfully graphed without a more carefully selected narrow range of useful pressures. Generally, a broad background is observed. This background is largely due to the luminescence of the diamond anvils. The presented data show remarkably linear pressure-induced shifts for both argon and krypton, as demonstrated in each of their least linear squares fit.

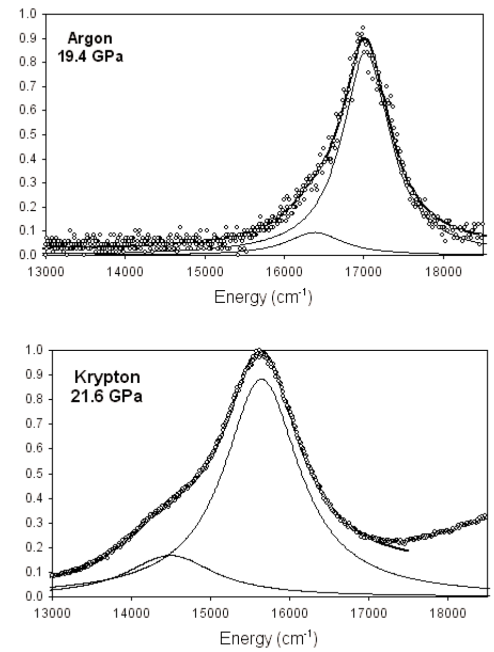

FIG. 1. Upper panel: Normalized Lorentzian peak fits of the argon luminescence at 19.4 GPa. Lower panel: Normalized Lorentzian peak fits of the krypton luminescence at 21.6 GPa. The broad background at higher energies (>18000 cm^{-1}) has not been fit in this figure.

It should be noted that there is, as yet, no underlying reason for this effect being linear over such a large pressure range.

For argon and krypton, the observed emission peaks are clearly a doublet. The two peaks for argon were fit [in units of wavenumbers (cm^{-1})] to 17900-43.6*P/GPa and 17300-47.5*P/GPa. Preliminary results for krypton yield the following equations: 18170-122.6*P/GPa and 17410-140.3*P/GPa. Interestingly, the red shift for krypton is nearly three times that for argon. Furthermore, there is a third peak observed from krypton that moves into the visible range above 35 GPa that also has a linear shift. This peak was fit to the equation 28970-209.2*P/GPa. The spectral changes are reversible without any hystereses in the peak shifts, intensities, and bandwidths.

Discussion

Due to the lack of investigations of this type, there is very little information about the luminescence of the condensed noble gases. However, the emission for argon has been reported to be due to excited neutral argon atoms.[1] At ambient pressure (and 20K) an ion bombardment study of argon using energies of 5 to 10 keV identified a peak at 560 nm to be the 4p-5d transition. If we extrapolate our results to ambient pressure, we find that our emission peak is at this position and matches the lineshape. Furthermore, we have detected no appreciable shift with temperature. This strongly suggests that our emission is from the 4p-5d transition as well. Unfortunately, there is no comparable study for krypton.

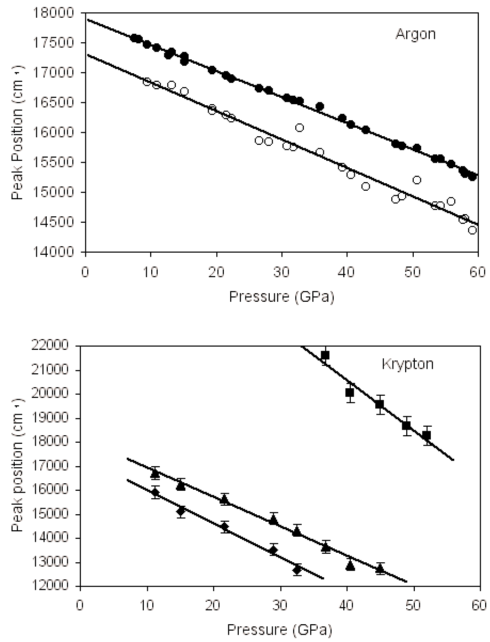

FIG. 2. Peak positions for the argon (upper panel) and krypton (lower panel) luminescence as a function of pressure. The linear fits are…
$E/cm^{-1} = 17897 - (43.64 * P)/GPa$, for the higher energy argon peak (solid circles)
$E/cm^{-1} = 17305 - (47.54 * P)/GPa$, for the lower energy argon peak (open circles)
$E/cm^{-1} = 18170 - (122.6 * P)/GPa$ for the doublet's higher energy krypton peak. (solid triangles)
$E/cm^{-1} = 17410 - (140.3 * P)/GPa$ for the doublet's lower energy krypton peak (solid diamonds)
$E/cm^{-1} = 28970 - (209.2 * P)/GPa$ for the highest observed energy peak from krypton (solid squares)

The linear shifts of the luminescence of argon and krypton are substantially greater than that of ruby, so this system can be used as an internal pressure standard. The visible luminescence of argon and krypton also provides a practical way of positioning x-rays for various high-pressure studies, including *in situ* laser-heated x-ray diffraction and x-ray spectroscopy at high pressures and temperatures. Using an intense 3rd-generation synchrotron source, x-ray induced luminescence could be applicable to many other systems such as f-centered alkali halides.

Acknowledgments

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